

# Supporting Information

## An EXAFS study on the reactions between iron and fulvic acid in acid aqueous solutions

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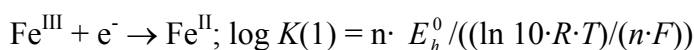
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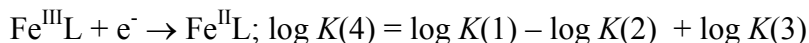
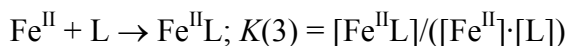
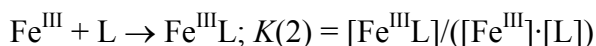
Number of figures: 4

## Stability of iron(II) and iron(III) complexes as a function of pH

In order to get a better understanding of the complex formation ability of different groups present in fulvic acid, the literature on effective stability constants of iron(II) and iron(III) complexes with different ligands was reviewed. The ligands investigated were acetic acid, phenol, phthalic acid, salicylic acid and catechol (no data were available for complexes of iron(II) with phenol and phthalic acid). The results of this literature review are summarised in Figure S1 and Figure 3 and show that iron(III) forms strong complexes with all the ligands investigated in the pH range 2-14. The complexes of iron(II) with these ligands are much weaker and complex formation starts at much higher pH. The bidentate ligand groups salicylic acid and phthalic acid form the strongest complexes with iron(III) at low pH, whereas at high pH the strongest complexes are formed with catechol and salicylic acid. Iron(II) forms the strongest complexes with acetic acid at low pH, and with catechol and salicylic acid at high pH. The standard electrode potential ( $E^0$ ) of the iron(III)/iron(II) couple in aqueous solution is given by the value when only water is bound to the ions, and the relative stability of a complex of iron(III) and iron(II) according to the formulae given below:

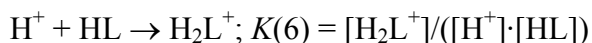
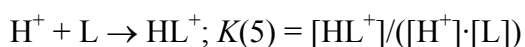


$$\Rightarrow \text{for iron(III)/iron(II) at } 25.0^\circ\text{C}; \log K(1) = 1 \cdot 0.7700 / 0.05916 = 13.016$$



$$\log K(4) = 1 \cdot E_h(\text{Fe}^{\text{III}}\text{L}/\text{Fe}^{\text{II}}\text{L}) / 0.05916 \Rightarrow E_h(\text{Fe}^{\text{III}}\text{L}/\text{Fe}^{\text{II}}\text{L}) = \log K(4) \cdot 0.05916$$

The effective stability constants are calculated in the following way:



$$\alpha_{\text{H}} = 1 + K(5) \cdot [\text{H}^+] + K(6) \cdot [\text{H}^+]^2$$

44  $K_E = K/\alpha_H$

45 The effective standard electrode potentials ( $E_h$ ) of the ( $\text{Fe}^{\text{III}}\text{L}$ )/( $\text{Fe}^{\text{II}}\text{L}$ ) couples as a function of pH  
46 for the different ligand complexes *versus* the normal hydrogen electrode are given in Figure 3.

47

48 These calculations show that all the systems studied have an approximate effective redox  
49 potential between +0.5V (reported redox potential of fulvic acid; 33,39) and +0.7V (reported redox  
50 potential of humic acid; 40) at pH = 2, while only the acetic acid and phenol systems have a redox  
51 potential higher than +0.5 V at pH = 4. This suggests that humic acid is not capable of reducing  
52 iron(III) even at a pH value of 2, which is consistent with our earlier findings (15). It might also  
53 explain the absence of iron(II) in the precipitate at pH 2, assuming the precipitate has an altered,  
54 increased redox potential in comparison to the dissolved fulvic acid.

55

**Table S1a.** Mean Fe-O bond distance,  $d(\text{Fe-O})/\text{\AA}$ , multiple scattering within the  $\text{FeO}_6$  core (double Fe-O bond distance),  $d(\text{FeO}_6)/\text{\AA}$ , and  $\text{Fe}\cdots\text{C}$  distance to bound carboxylate and phenolate group,  $d(\text{Fe}\cdots\text{C})/\text{\AA}$ , and the corresponding Debye-Waller factor coefficients,  $\sigma^2/\text{\AA}^2$ , in aqueous solution of iron(III) and fulvic acid at pH 2 after different storage times. The 3-leg multiple Fe-O-C scattering path is approx. 0.2  $\text{\AA}$  longer than the given  $d(\text{Fe}\cdots\text{C})$  distance. The calculations were performed on EXAFS data in the  $k$ -range 2-10  $\text{\AA}^{-1}$ .  $E_0$  denotes the energy of the first inflection point and  $S_0^2$  the amplitude reduction factor

Sample age	$N$	$d(\text{Fe-O})$ $\text{\AA}$	$\sigma^2$ $\text{\AA}^2$	$E_0$ $\text{eV}$	$S_0^2$	$d(\text{FeO}_6)$ $\text{\AA}$	$\sigma^2$ $\text{\AA}^2$	$d(\text{Fe}\cdots\text{C})$ $\text{\AA}$	$\sigma^2$ $\text{\AA}^2$
15 minutes	6	1.984(6)	0.0072(6)	7121.5(3)	0.87(6)	3.95(3)	0.021(3)	2.95(2)	0.010(2)
24 hours	6	1.987(7)	0.0109(8)	7121.5(3)	0.90(7)	3.95(3)	0.020(3)	2.98(2)	0.011(2)
48 hours	6	2.007(5)	0.0081(8)	7119.0(3)	0.83(5)	4.00(3)	0.021(3)	3.00(2)	0.010(2)
7 days	6	2.035(15)	0.0096(9)	7118.7(3)	0.85(6)	4.05(4)	0.021(3)	3.05(2)	0.013(2)
30 days	6	2.068(11)	0.0092(10)	7118.5(3)	0.85(5)	4.11(4)	0.023(3)	3.12(2)	0.014(2)
12 months	6	2.098(8)	0.014(3)	7118.1(3)	0.84(4)	4.18(3)	0.025(3)	3.15(2)	0.018(2)
34 months	6	2.107(10)	0.0111(14)	7118.2(3)	0.86(4)	4.20(3)	0.025(3)		
Solid/34 months	6	2.007(7)	0.0081(8)	7121.5(3)	0.086(6)	3.98(3)	0.020(3)	*	

\*  $d(\text{Fe}\cdots\text{Fe}) = 3.30(2) \text{\AA}$      $\sigma^2 = 0.050(1) \text{\AA}^2$

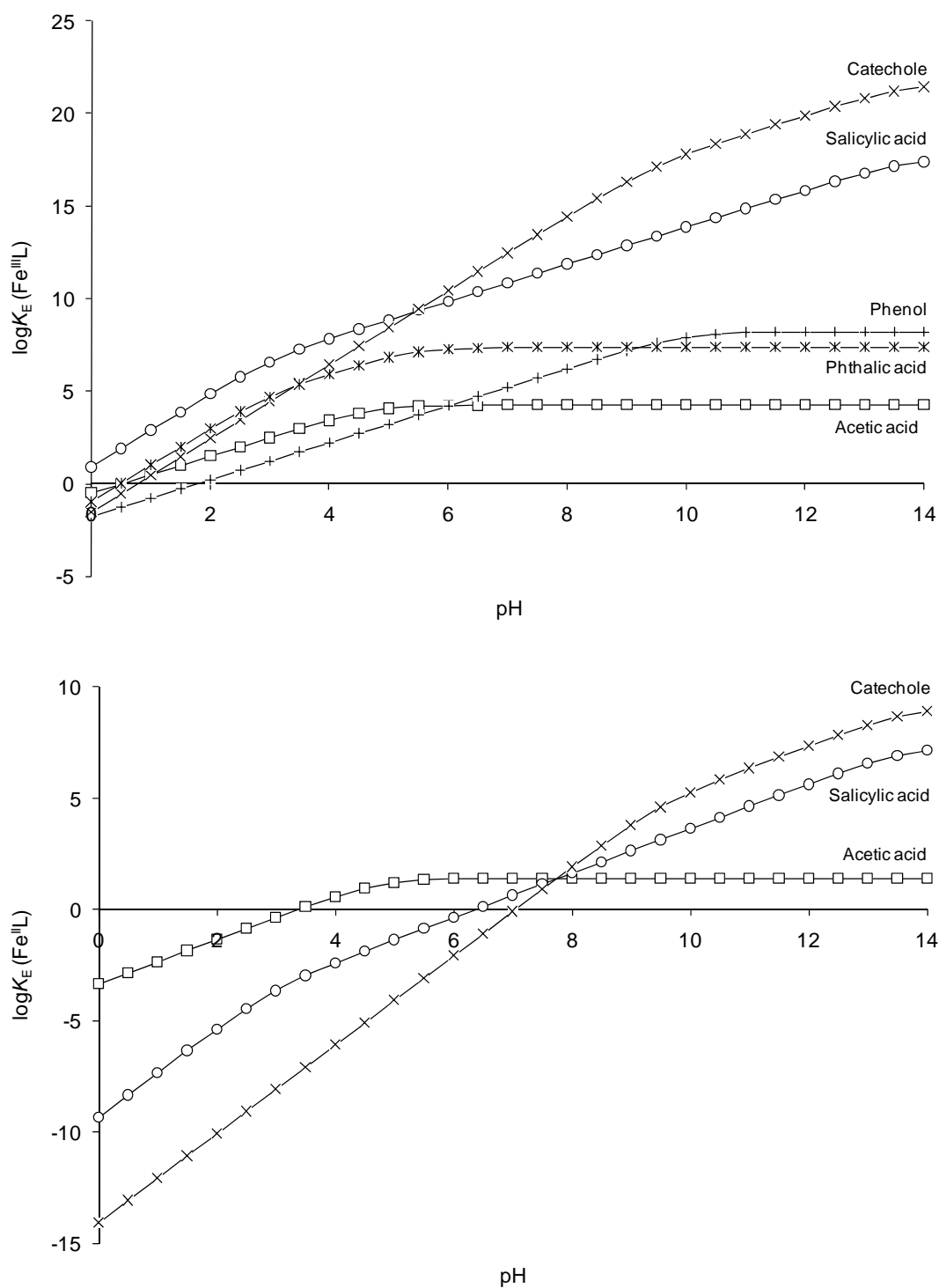
**Table S1b.** Mean Fe-O bond distance,  $d(\text{Fe-O})/\text{\AA}$ , multiple scattering within the  $\text{FeO}_6$  core (double Fe-O bond distance),  $d(\text{FeO}_6)/\text{\AA}$ , and  $\text{Fe}\cdots\text{C}$  distance to bound carboxylate and phenolate group,  $d(\text{Fe}\cdots\text{C})/\text{\AA}$ , and the corresponding Debye-Waller factor coefficients,  $\sigma^2/\text{\AA}^2$ , in aqueous solution of iron(III) and fulvic acid at pH 4 after different storage times. The 3-leg multiple Fe-O-C scattering path is approx. 0.2  $\text{\AA}$  longer than the given  $d(\text{Fe}\cdots\text{C})$  distance. The calculations were performed on EXAFS data in the  $k$ -range 2-10  $\text{\AA}^{-1}$ .  $E_0$  denotes the energy of the first inflection point and,  $S_0^2$  the amplitude reduction factor

Sample age	$N$	$d(\text{Fe-O})$ $\text{\AA}$	$\sigma^2$ $\text{\AA}^2$	$E_0$ eV	$S_0^2$	$d(\text{FeO}_6)$ $\text{\AA}$	$\sigma^2$ $\text{\AA}^2$	$d(\text{Fe}\cdots\text{C})$ $\text{\AA}$	$\sigma^2$ $\text{\AA}^2$
15 minutes	6	1.987(5)	0.0058(6)	7122.2(3)	0.85(5)	3.95(3)	0.020(3)	2.98(2)	0.011(2)
24 hours	6	1.982(6)	0.0074(6)	7121.5(3)	0.87(6)	3.95(3)	0.021(3)	2.98(2)	0.010(2)
48 hours	6	1.987(9)	0.0109(8)	7121.5(3)	0.90(7)	3.95(3)	0.019(3)	2.96(2)	0.011(2)
7 days	6	1.997(8)	0.0098(8)	7121.3(3)	0.88(6)	3.99(3)	0.019(3)	2.95(2)	0.011(2)
30 days	6	2.011(8)	0.0086(7)	7120.9(3)	0.84(6)	3.99(4)	0.020(3)	2.92(3)	0.012(3)
12 months	6	2.014(8)	0.0092(7)	7120.5(3)	0.85(5)	4.02(3)	0.020(3)	2.85(4)	0.014(3)
28 months	6	2.026(6)	0.0098(8)	7119.9(3)	0.87(4)	4.04(3)	0.024(3)	2.82(5)	0.015(4)

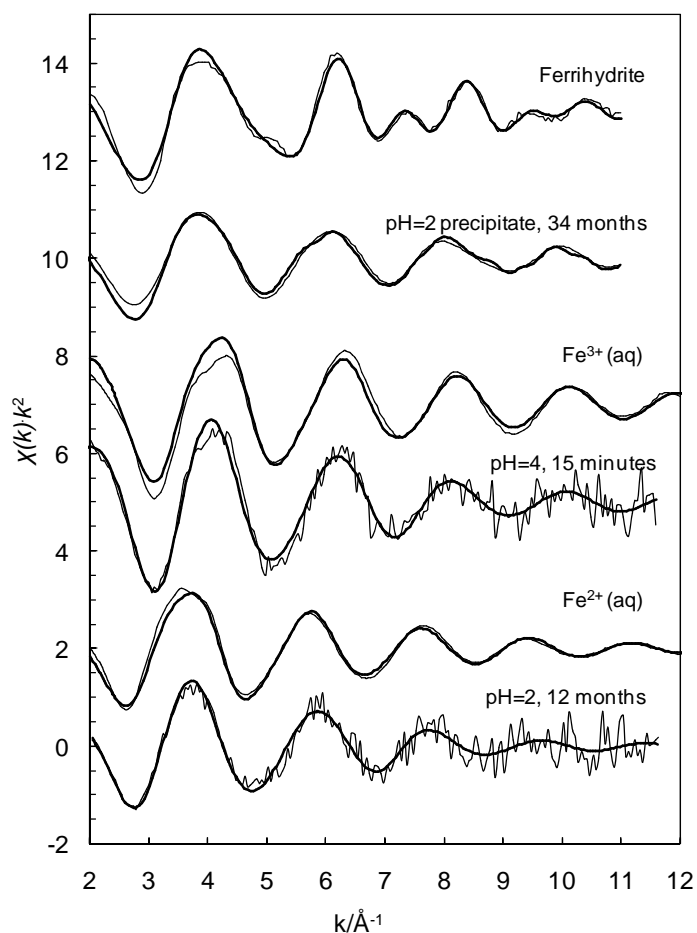
**Table S2.** Model ligands and stability constants used for calculation of the effective electrode potential for the  $\text{Fe}^{\text{III}}\text{L}/\text{Fe}^{\text{II}}\text{L}$  redox pair

Model Ligand (L)		$\log K^a$
Phenol	HL	9.997
	$\text{Fe}^{\text{III}}\text{L}$	8.2
	$\text{Fe}^{\text{II}}\text{L}$	-
Acetic acid	HL	4.757
	$\text{Fe}^{\text{III}}\text{L}$	4.24
	$\text{Fe}^{\text{II}}\text{L}$	1.4
Catechol	HL	13.7
	$\text{H}_2\text{L}$	23.18
	$\text{Fe}^{\text{III}}\text{L}$	21.62
	$\text{Fe}^{\text{II}}\text{L}$	9.09
Salicylic acid	HL	13.7
	$\text{H}_2\text{L}$	16.672
	$\text{Fe}^{\text{III}}\text{L}$	17.55
	$\text{Fe}^{\text{II}}\text{L}$	7.33
Phthalic acid	HL	5.411
	$\text{H}_2\text{L}$	8.361
	$\text{Fe}^{\text{III}}\text{L}$	7.36
	$\text{Fe}^{\text{II}}\text{L}$	-

<sup>a</sup> NIST Standard Reference Database 46, <http://www.nist.gov/srd/nist46.htm>. (37)

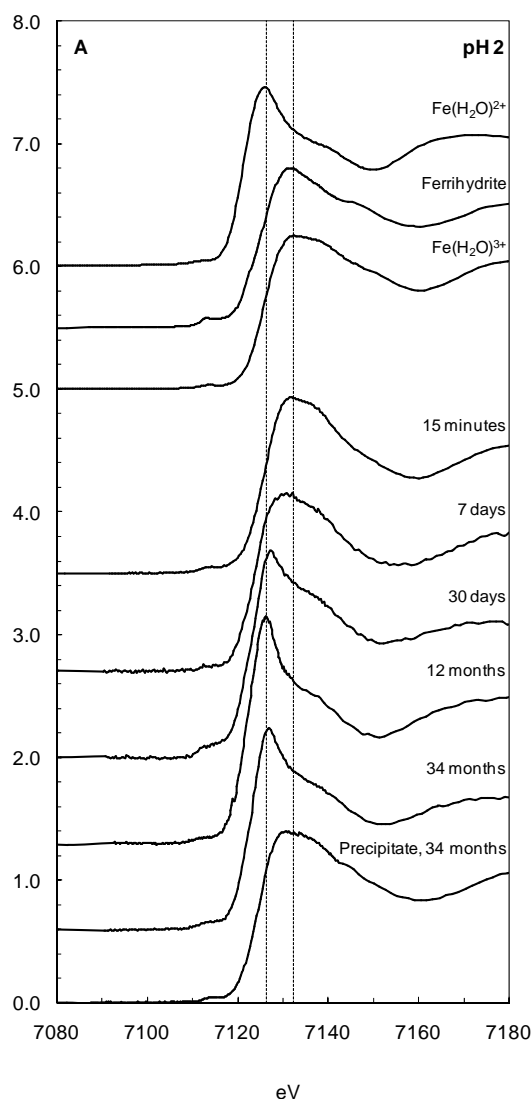


**Figure S1.** The effective stability constants ( $K_E$ ) of iron(III) (upper diagram) and iron(II) (lower diagram) complexes with acetic acid, phenol, phthalic acid, salicylic acid and catechol as a function of pH.

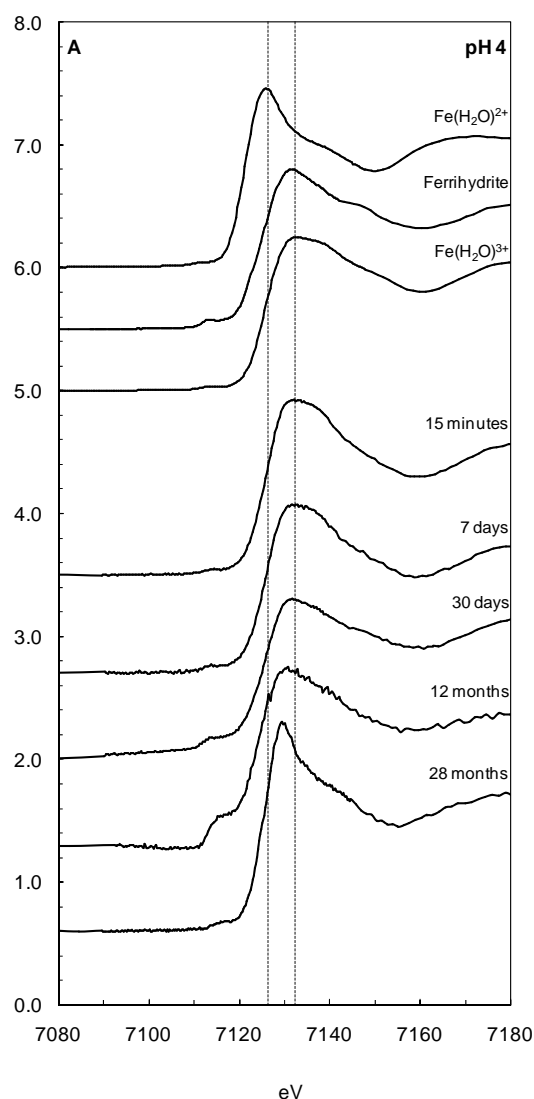


**Figure S2.**  $k^2$ -weighted EXAFS spectra for iron in the pH 2 (12 months, no offset) and in the pH 4 (15 minutes, offset +5.0) sample. Reference spectra for hydrated iron(III) (offset +7.0) and iron(II) (offset +2.0) ions in aqueous solution are included for comparison, as well as the spectra for the pH 2 precipitate (offset +10.0) and synthetic ferrihydrite (offset +13.0). Thin and thick lines represent the experimental data and best fits, respectively.

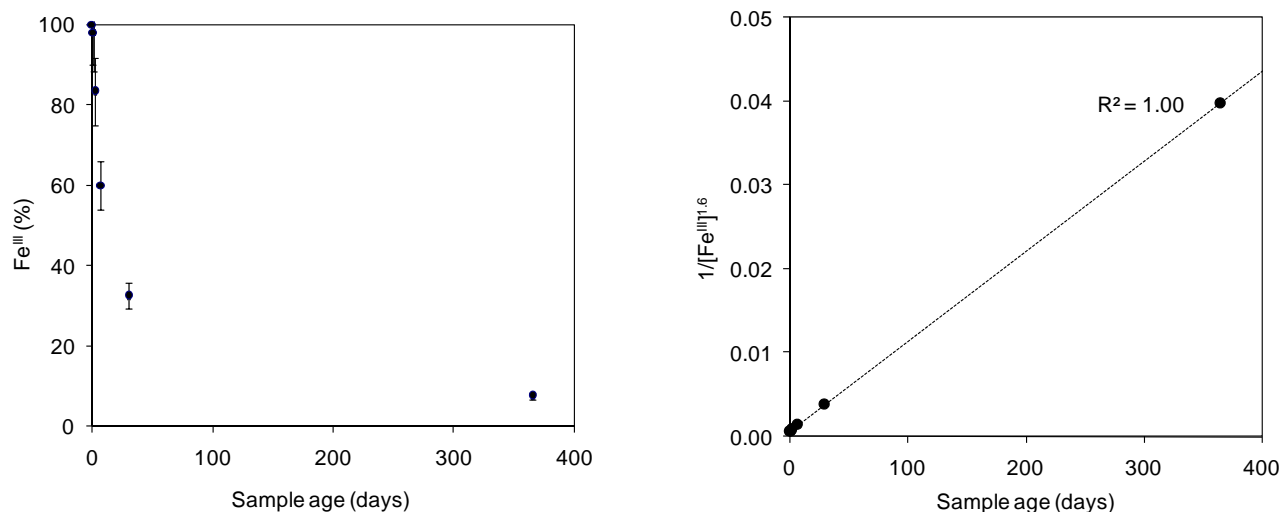




**Figure S3a.** XANES spectra of the aqueous iron(III)-fulvic acid solution at pH 2; newly prepared (offset 3.5), 7 days old (offset 2.7), 30 days old (offset 2.0), 12 months old (offset 1.3), 34 months old (offset 0.6) and solid precipitated after 34 months (no offset). Reference spectra of the hydrated iron(II) (offset 6.0) and iron(III) (offset 5.0) ion in aqueous solution and solid ferrihydrite (offset 5.5) are given for comparison.



**Figure S3b.** XANES spectra of the aqueous iron(III)-fulvic acid solution at pH 4; newly prepared (offset 3.5), 7 days old (offset 2.7), 30 days old (offset 2.0), 12 months old (offset 1.3) and 28 months old (offset 0.6). Reference spectra of the hydrated iron(II) (offset 6.0) and iron(III) (offset 5.0) ion in aqueous solution and solid ferrihydrite (offset 5.5) are given for comparison.



**Figure S4.** Estimates of iron(III) as percentage of total iron (left) and empirically determined reaction order kinetics (right), as derived from EXAFS data, versus age of the sample at pH 2. Note that error bars of 10% were used to indicate the relatively high inaccuracy of this approach. Nonetheless the figure clearly indicates that the reduction of iron(III) to iron(II) conforms to higher order kinetics. From the figure it follows that the equation  $(d\text{Fe}^{\text{III}}/dt) = k \cdot [\text{Fe}^{\text{III}}]^x$  yields a linear result for  $x = 2.6$ , with  $[\text{Fe}^{\text{III}}]$  the estimated amount of iron(III) as percentage of total iron. The fraction of Fe(III) was obtained from the Fe-O distances given in Table S1a, assuming that the shift in Fe-O bond distance can be directly related to the percentage of initially present iron(III) reduced to iron(II).